Electrolytes - Advanced Electrolyte and Electrolyte Additives

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DOE merit review

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Project ID# ES066

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Overview

Timeline

- Start: April 1, 2009
- Finish: Sept. 30 2014
- 40%

Barriers

- Barriers addressed
  - Cycle life
  - Calendar life
  - Abuse tolerance

Budget

- Total project funding
  - DOE share: $1200 K
  - Contractor share
- FY10: $ 300 K
- FY11: $ 300 K

Partners

- Interactions/ collaborations
  - Enerdel®, A123®, JC_Saft
  - Central Glass®
  - Grant Smith, University of Utah
  - Kevin Gering, INEL

Objectives

- An integrated theoretical/experimental program to understand how electrolyte additives work and find new ones for increased cycle life, calendar life, safety of lithium ion batteries
- Develop advanced quantum chemical models to understand and predict functional additives that form stable Solid Electrolyte Interphase (SEI) on anodes and cathodes as well as shuttles for overcharge protection
  - Past year: increase database of additive candidates for anode SEI formation; screening for promising initial decomposition pathways; insight into new experimental additives
- Experimental studies of new additives for protective SEI formation and shuttles for overcharge protection
  - Past year: synthesis of new organic additives; investigation of modification of salts as additives; testing performance of new additives for anode SEI's including impedance and cycle life

Approach

Search for new electrolyte materials that react in a preferential manner to prevent detrimental decomposition of other cell components

Theoretical methods

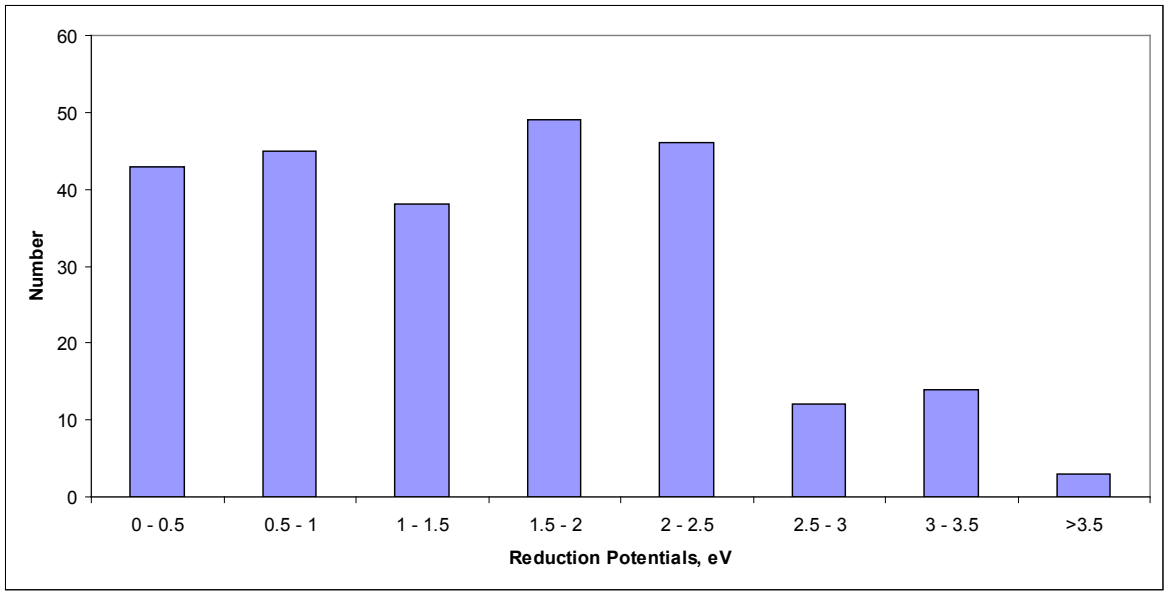
- Accurate quantum chemical calculations of energies to obtain reduction and oxidation potentials, reaction energies, barriers
- Density functional theory (B3LYP); very high accuracy Gn theories
- Continuum model for solvation effects
- Multi-scale modeling: collaboration with Grant Smith (Utah)
  - Provide accurate quantum chemical data for use in more approximate modeling at larger scales

Experimental methods

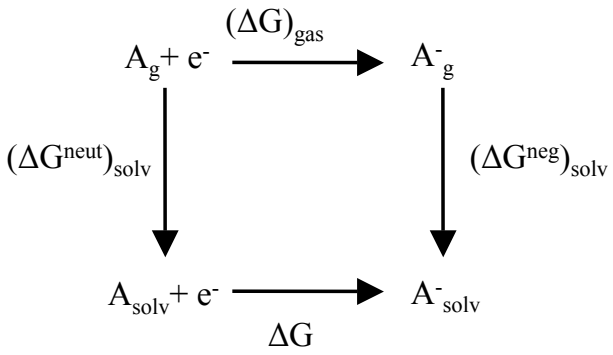
- Cycle life testing
- Impedance testing
- Organic synthesis of new additives

Accomplishment: Screening of reduction potentials of over 275 additive candidates

- **Bar chart shows the distribution of the reduction potentials relative to Li electrode of more than 275 candidate additives; information on the candidates is stored in a database**



Thermodynamic Cycle Used to Calculate Reduction Potentials

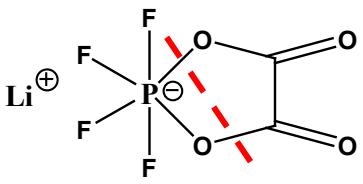


$$\Delta G = (\Delta G)_{gas} + (\Delta G^{neg})_{solv} - (\Delta G^{neut})_{solv}$$

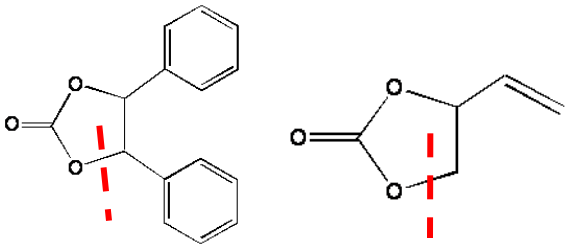
- **More than 160 candidate additives have favorable reduction potentials of greater than 1 eV**

Accomplishment: Screening for initial decomposition step after reduction

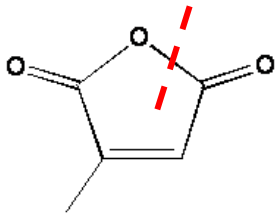
- **Screening of candidates in the database has so far found four groups of molecules with possible favorable decomposition mechanisms**



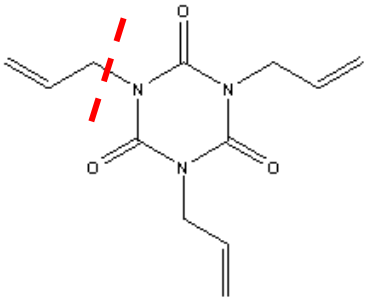
Oxalates (4)



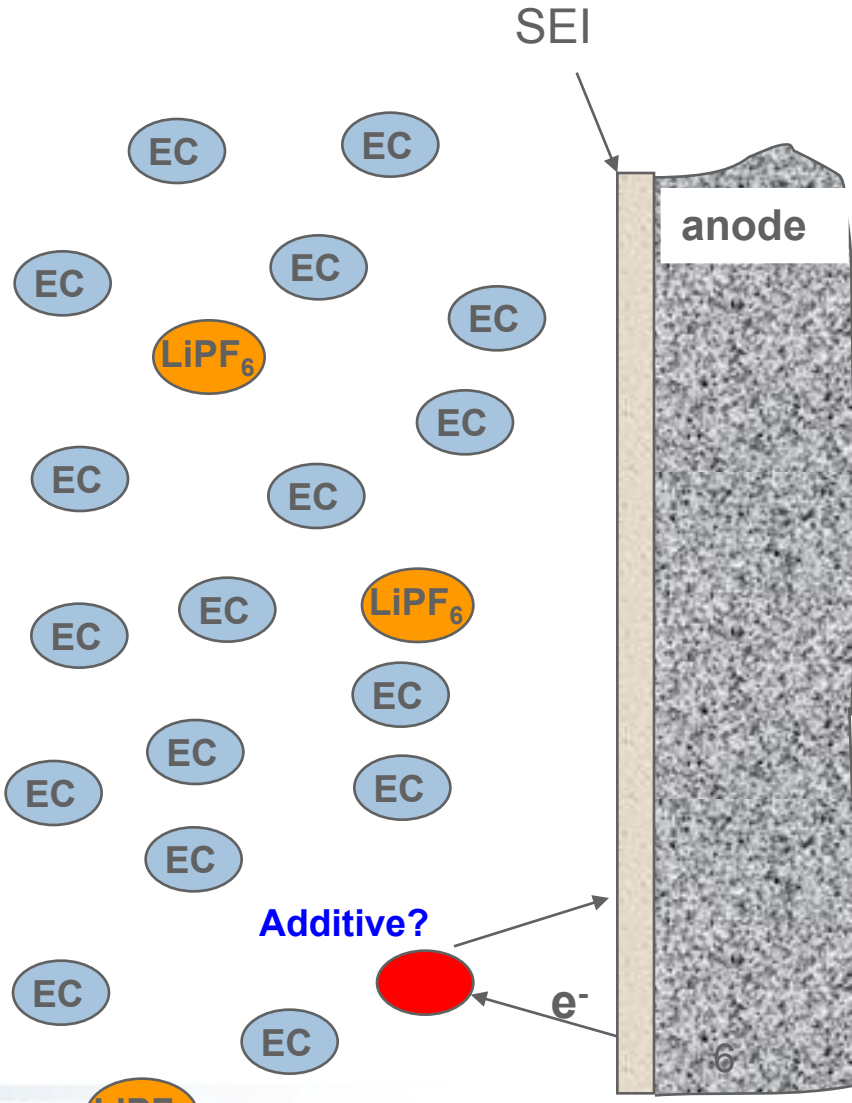
Carbonates (52)



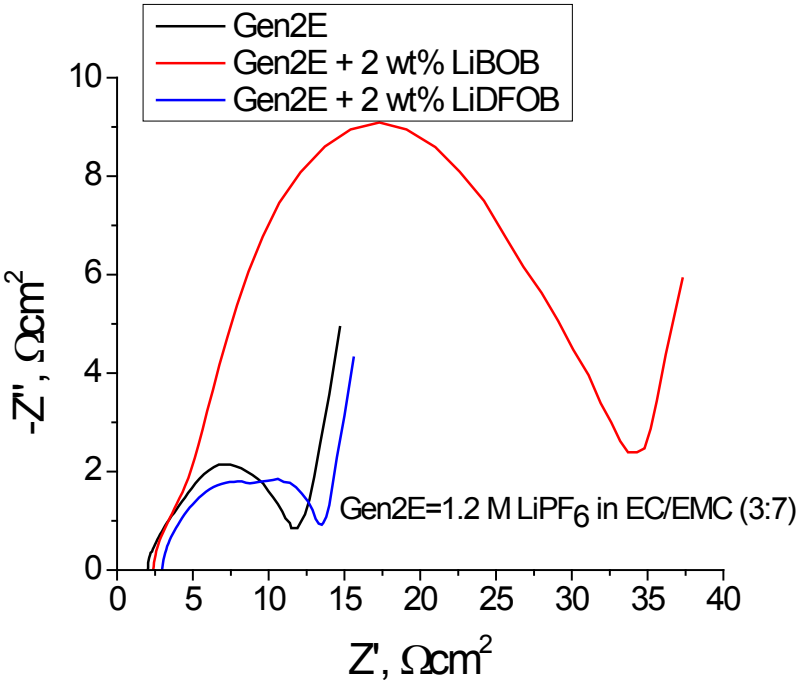
Anhydrides (19)

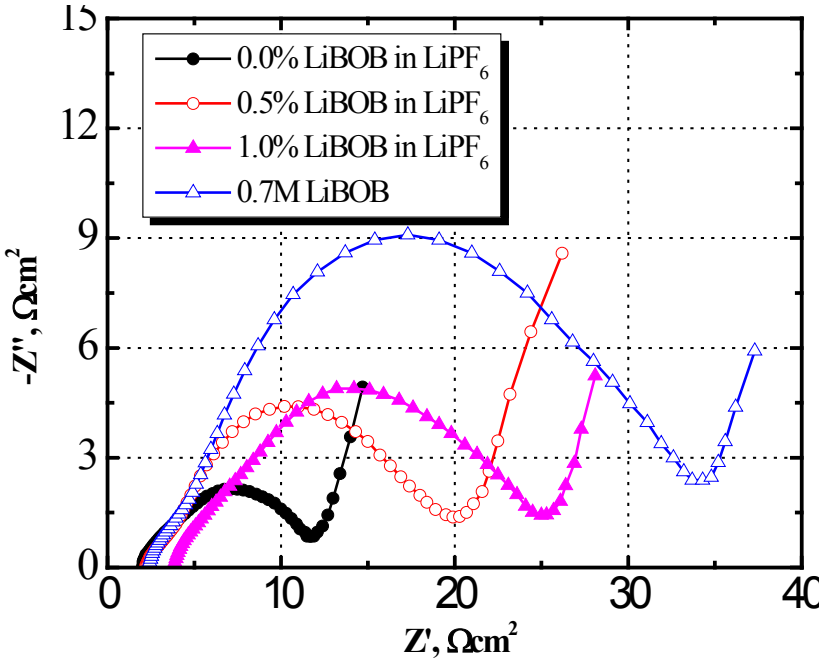


Allyl-substituted rings (2)



Accomplishment: Investigation of impedance of SEI films formed from LiBOB and LiDFOB



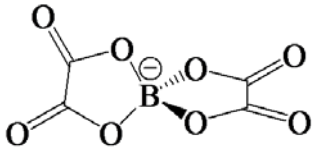


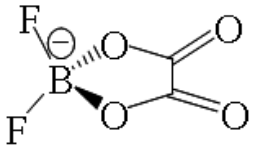
AC impedance of MCMB/Li1,1[Mn1/3Ni1/3Co1/3]0.9O_2 lithium-ion cells using different electrolytes showing the advantage of LiDFOB over LiBOB. The baseline electrolyte is 1.2 M LiPF6 in EC/EMC (3:7 by weight).

AC impedance of MCMB/Li1,1[Mn1/3Ni1/3Co1/3]0.9O2 lithium-ion cells using different electrolytes.

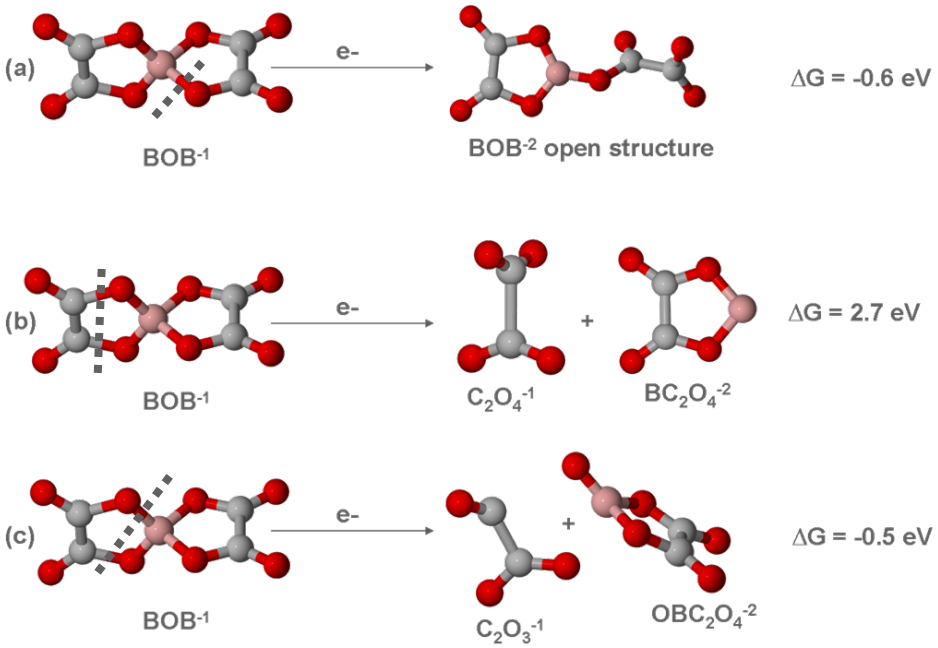
After tested at 55C for 1000 cycles, the cell with 2 wt% LiDFOB still had 78 % capacity retention, while the cell without LiDFOB addition lost about 25 % reversible capacity after 80 cycles

Accomplishment: Calculation of some possible first decomposition steps of LiBOB and LiDFOB

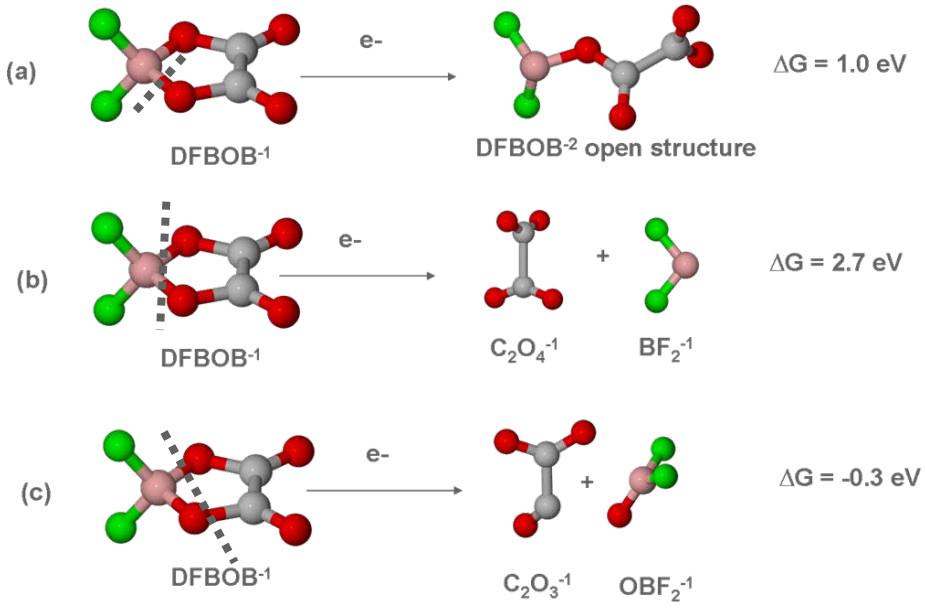




$[LiB(C_2O_4)_2]$ reduction reactions

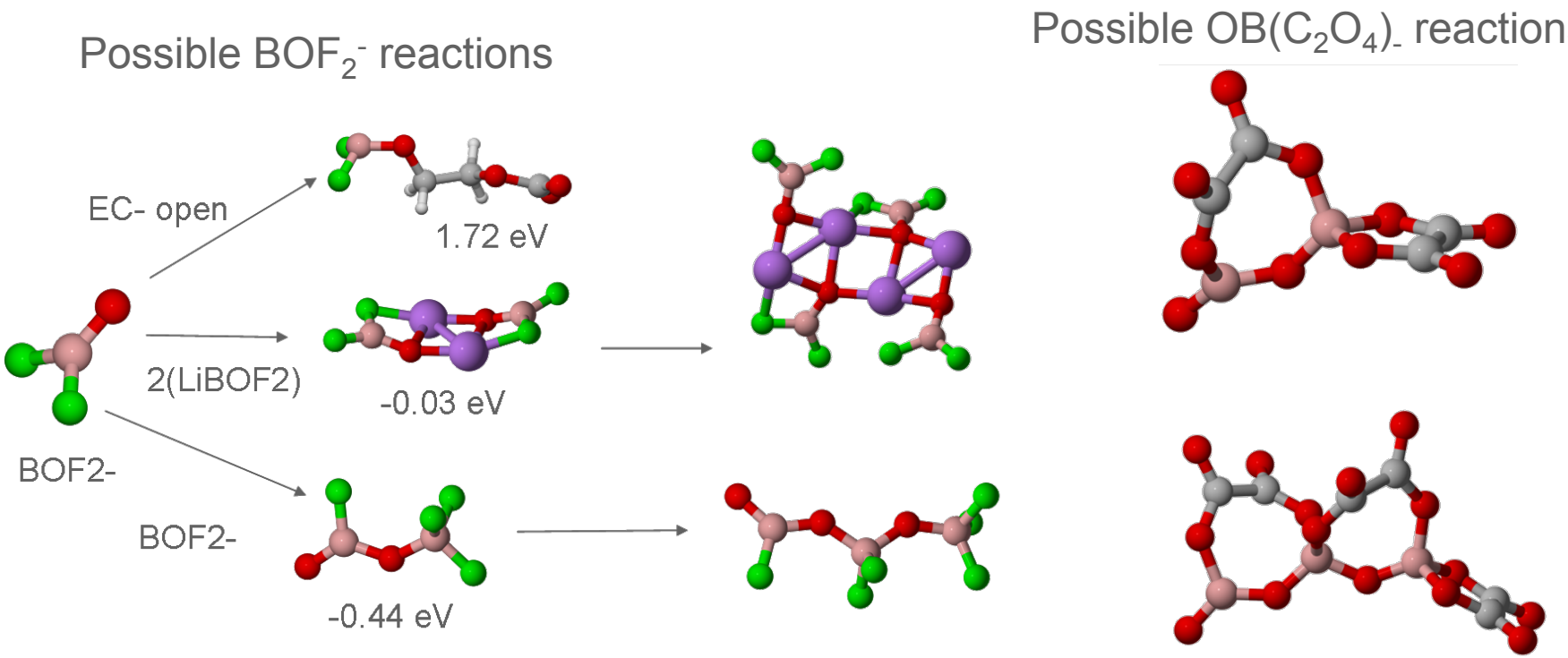


$[LiBF_2(C_2O_4)]$ reduction reactions



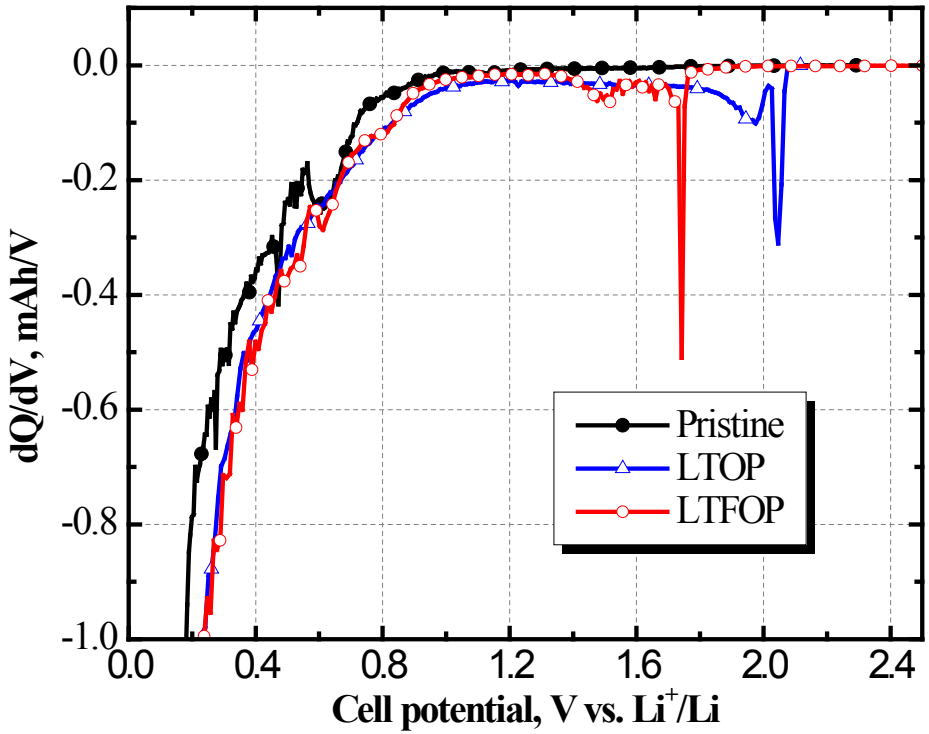
- **(a) and (c) are possible reaction occurring upon reduction of BOB anion**
- **(c) is the most likely reaction occurring upon reduction of DFOB anion**

Accomplishment: Calculation of possible first decomposition steps of LiBOB and LiDFOB



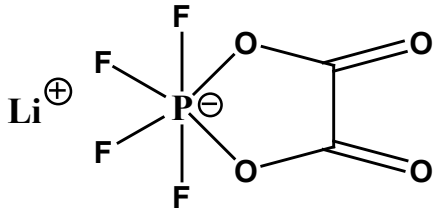
- **Calculations indicate that fluorine substitution results in products, which could lead to polymeriztion, that are more 2-dimensional than the BOB products**
- **Could be responsible for thinner films and lower impedance**

Accomplishment: Improved performance by salt additives – LTOP, LTFOP



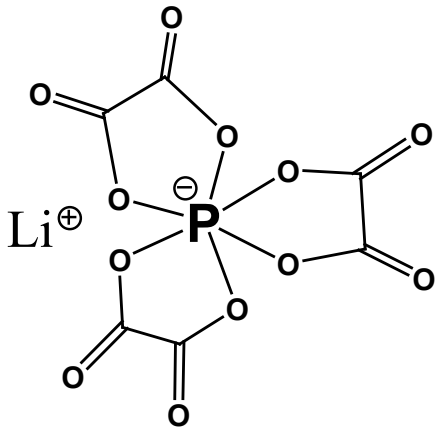
Li/Graphite half cell differential capacity profiles
Electrolyte: 1.2M $LiPF_6$ EC/EMC 3/7+2% additive

lithium tetrafluoro(oxalate) phosphate (LTFOP)



Red. Pot: 1.7V *vs* Li^+/Li)
Theory: 1.5 eV

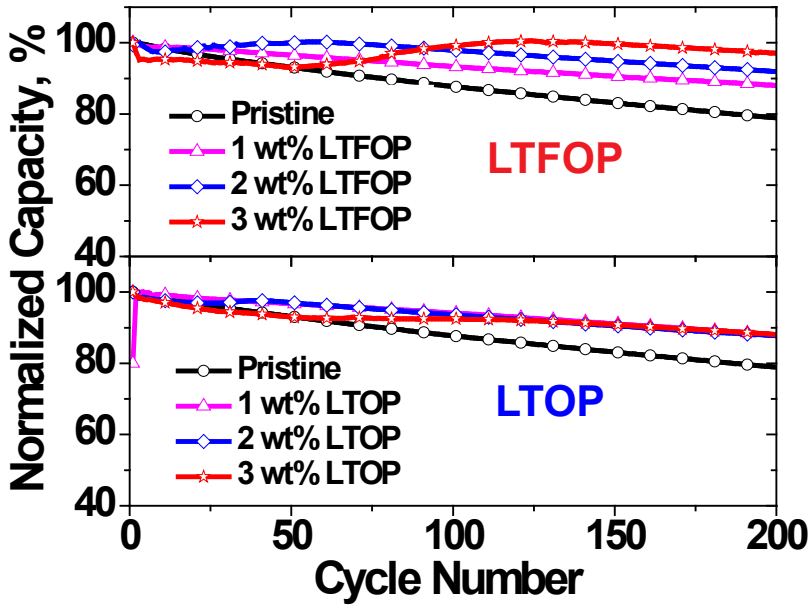
lithium tris(oxalato) phosphate (LTOP)



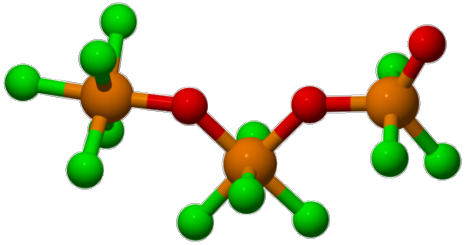
Red. Pot.: 2.1V *vs* Li^+/Li)
Theory: 1.9 eV

Accomplishment: Improved performance by salt additive – LTOP, LTFOP

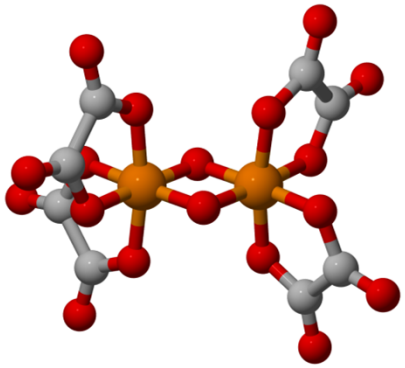
1C rate for cycling at 55°C



DFT calculations of possible initial polymerization steps



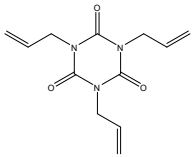
trimer from LFTOP fragmentation product

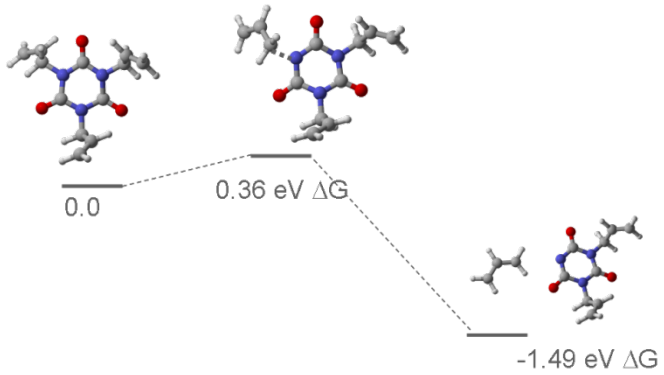


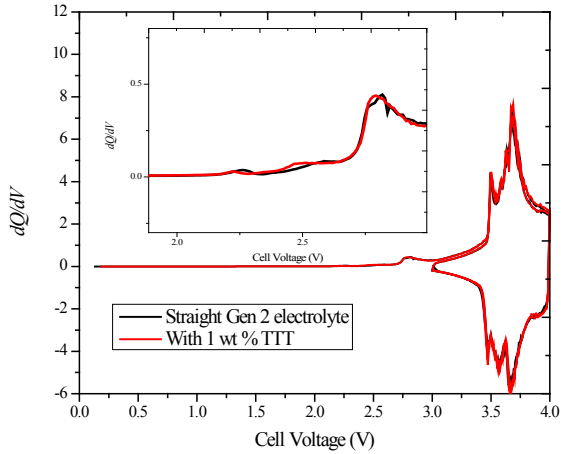
dimer from LTOP fragmentation product

- Addition of 1~3 wt% LTFOP improves the cycle life, 3% shows the best result.
- More additive decreases the capacity due to thicker SEI layer formation.
- Addition of 1~3 wt% LTOP shows the similar improvement on the cycle life.

Accomplishment: Differential capacity profiles of 1,3,5-triallyl-1,3,5-triazinane-2,4,6-trione (TTT) and Gen 2 electrolyte



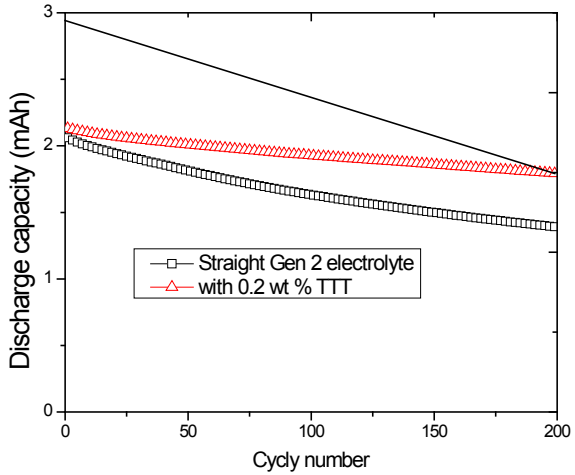




55°C

- **Predicted favorable decomposition**

Diff. Capacity vs voltage of MCMB 1028/$Li_{1.1}[Ni_{1/3}Co_{1/3}Mn_{1/3}]0.9O_2$ coin cells in 3E7EMC/PF12 with or without 1 wt% additives. The cells were cycled at 55 ◦C. The charge rate was C/10. The cut-off voltages were 3 ~ 4 V.



Capacity retention of MCMB-1028/$Li_{1.1}[Ni_{1/3}Co_{1/3}Mn_{1/3}]_{0.9}O_2$ coin cells in 3E7EMC/PF12 with or without 1 wt% additives. The cells were cycled at 55 ◦C. The charge rate was 1C. The cut-off voltages were 3~4 V.

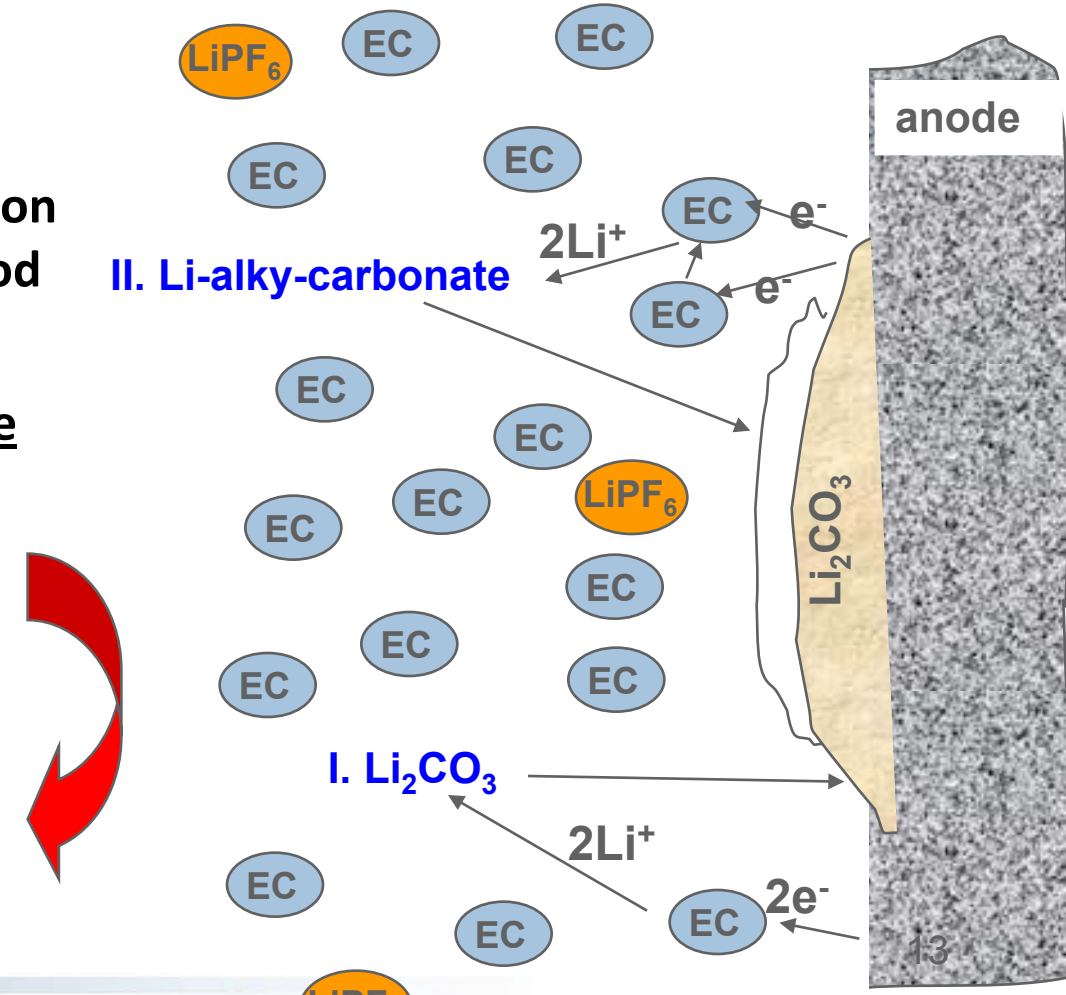
- TTT shows improved performance as an additive; nature of SEI needs further investigation

Accomplishment: Investigation of reaction pathways for ethylene carbonate (EC) reactions for lithium alkyl formation including reaction barriers

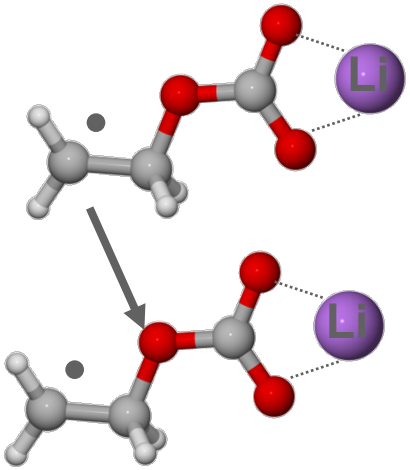
- Lithium carbonate formation 2-electron transfer mechanism (I) well-studied
- Lithium alkyl carbonate formation mechanism (II) is less understood

Collaborative effort on multi-scale modeling of SEI formation

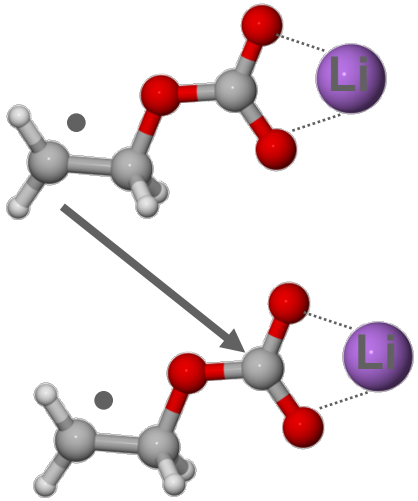
- Accurate quantum chemical calculations with continuum model for solvent (this project)
- Force fields for MD simulations (Smith, Utah)



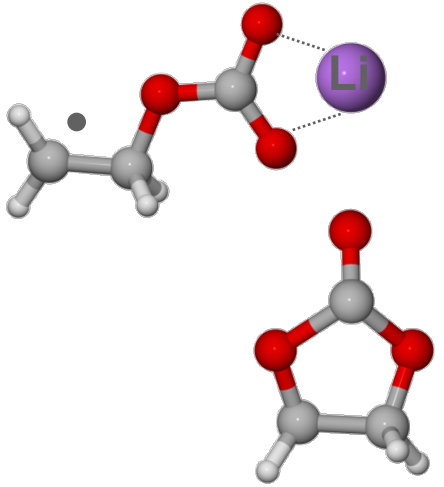
Accomplishment: Investigation of reaction pathways for different possible EC reduced species



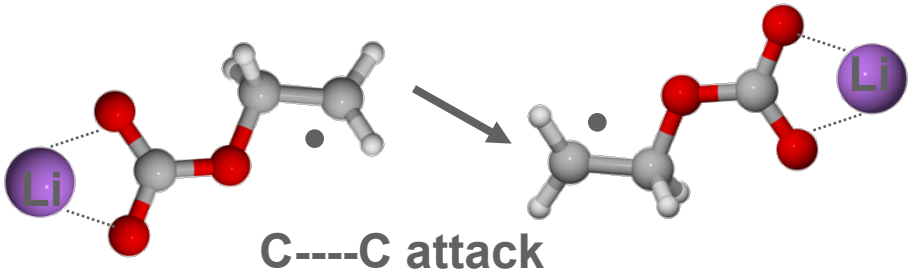
C----O attack



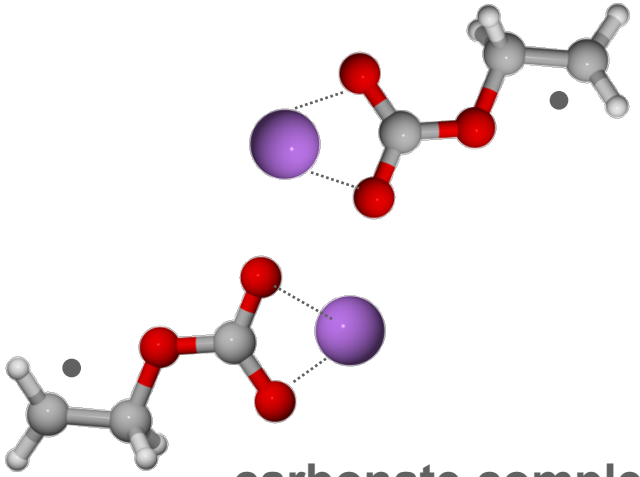
C- carboxyl attack



2-electron reduction

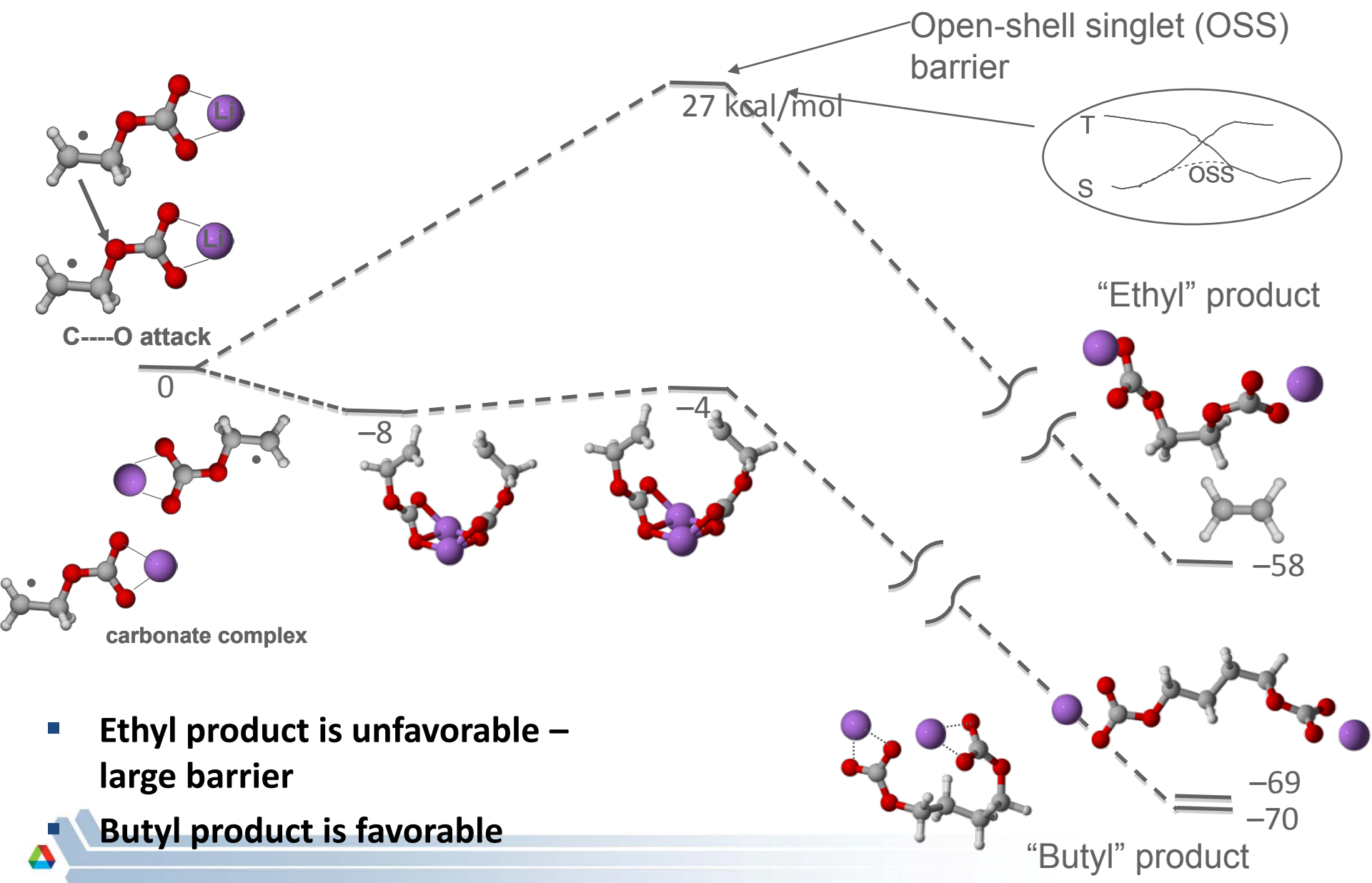


C----C attack



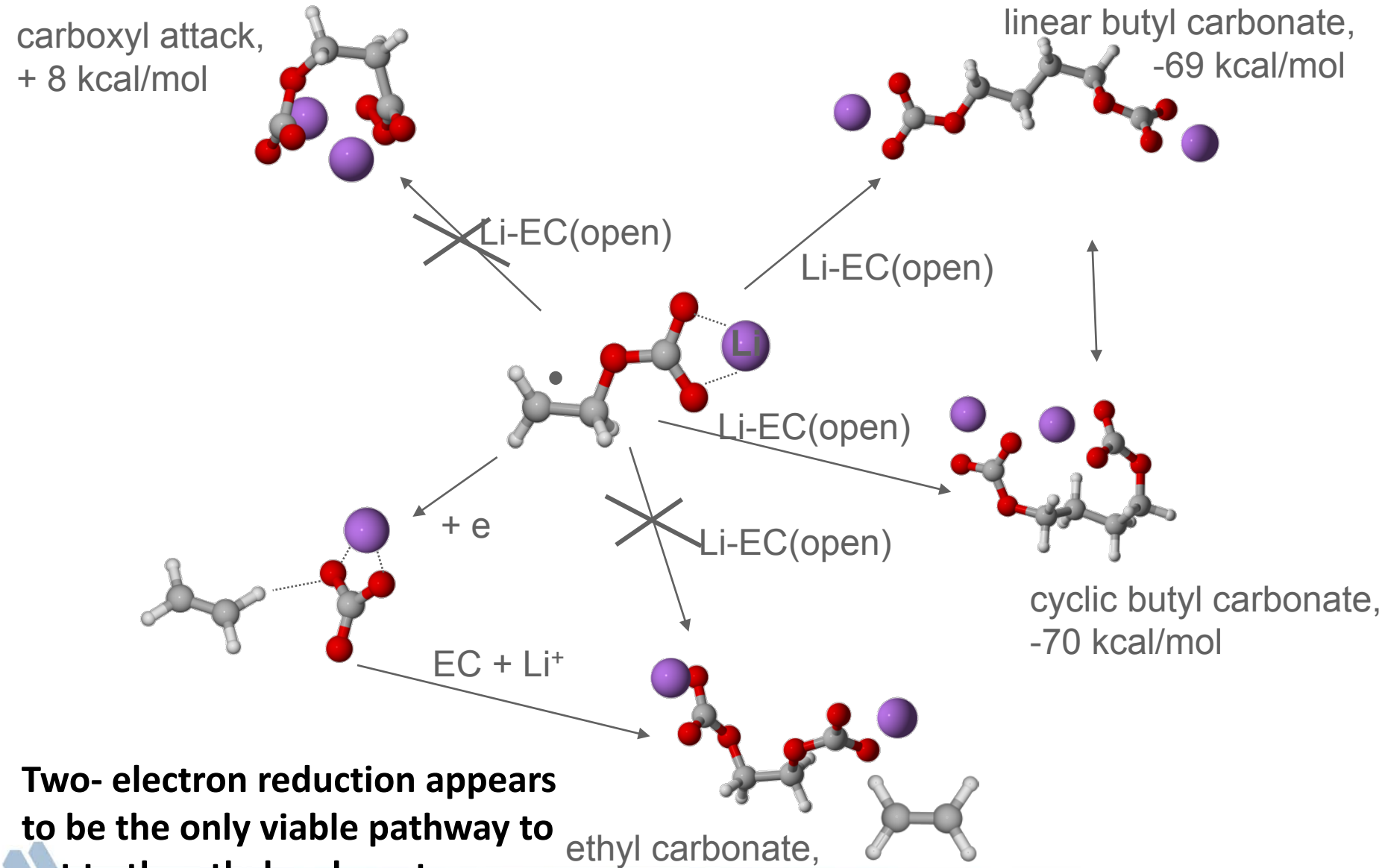
carbonate complex

Accomplishment: Determination of singlet/triplet and open-shell singlet reaction barrier for reaction of two EC open radicals



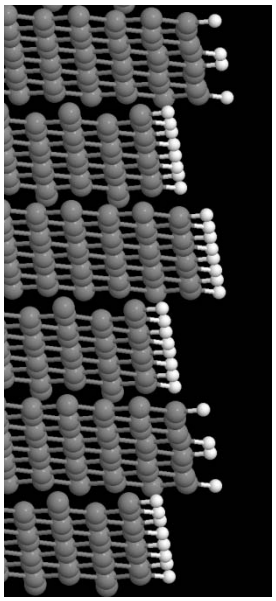
- **Ethyl product is unfavorable – large barrier**
- **Butyl product is favorable**

Accomplishment: Assessment of most favorable pathways to get to “ethyl” carbonate

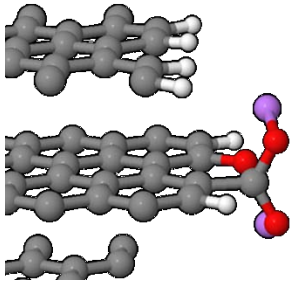


- **Two- electron reduction appears to be the only viable pathway to get to the ethyl carbonate**

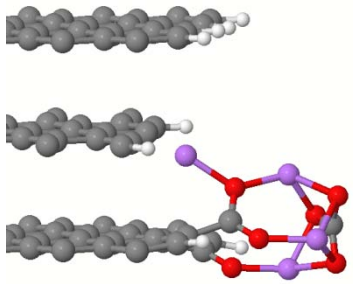
Accomplishment: DFT Investigation of Li_2CO_3 growth structures on a graphite edge surface



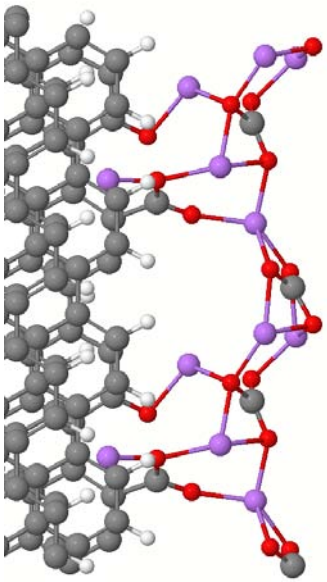
graphite



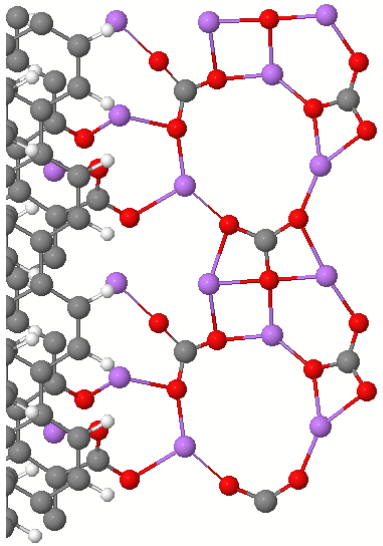
monomer



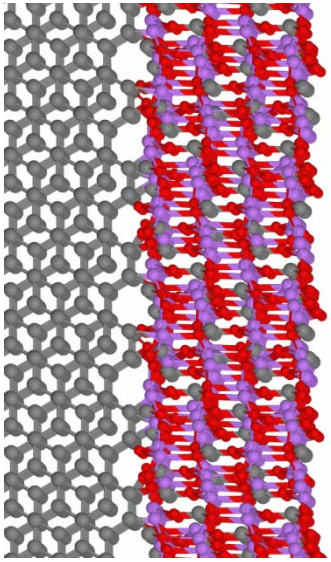
dimer



trimer



tetramer



- **Many structures investigated for adsorbates**
- **Defect sites (missing hydrogens) on the graphite edges are very reactive towards Li_2CO_3 and are likely nucleation sites for lithium carbonate SEI growth.**

Collaborators

- Industrial Partners
  - Validation of additives in a full cell configuration
    - Enerdel, A123, JC-Saft
  - Materials
    - Central Glass
- Collaborators
  - Grant Smith (university of Utah)
    - Multi-scale modeling: provide accurate quantum chemical data for use in more approximate modeling at larger scales
  - Kevin Gering (INEL)
    - Modeling conductivity
  - Y. K. Sun (Hanyang University, Korea)
    - Synthesis
  - University of Utah
    - XPS measurements
- ANL contributors
  - Experiment: Z. Zhang, Z. Chen
  - Theory: P. Redfern, H. Iddir, G. Ferguson

Proposed Future Work

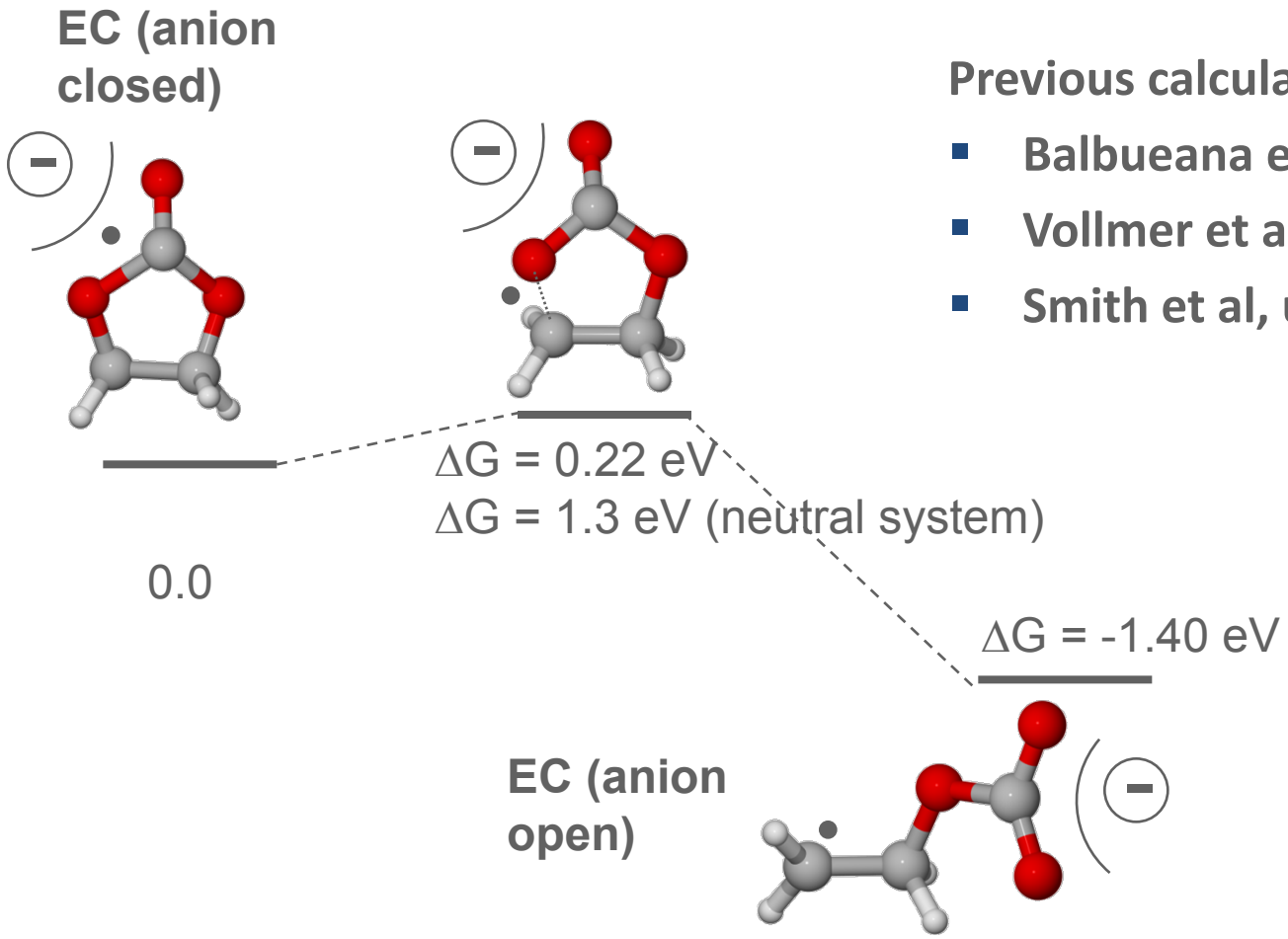
- Understanding and prediction of new additive materials from our database of candidate species based on screening of reduction potentials
  - Focus will be on improved modeling of decomposition reaction pathways leading to SEI formation
  - Improved solvation models – inclusion of explicit water molecules
  - Collaboration with Grant Smith (Utah) to integrate high level quantum chemical studies with larger scale methods for modeling SEI formation mechanisms
  - Characterization of SEI
- Synthesis of new additive materials based on theoretical predictions
- Testing of new additive materials
- Extend methods to shuttles for overcharge protection

Summary

- Improved quantum chemical model for the calculation of reduction potentials
  - Screening of over 275 candidate materials
- Further screening based on initial decomposition pathways has identified 77 new promising candidates
  - carbonates, oxalate salts, anhydrides, allyl- substituted species.
- Experimental studies on new additives
  - improved performance
    - LiDFOB, LiBOB
    - LFTOP, LTOP
    - Allyl substituted rings species
- New insight into lithium alkyl formation from ethylene carbonate

Extra slides

Accomplishment: High level G4 theory calculation of ring opening of ethylene carbonate upon reduction



Previous calculations

- Balbueana et al JACS
- Vollmer et al JECS
- Smith et al, unpublished

- Reduction potential of EC is 1.52 eV to the open form
- Reaction barrier to open anion radical difficult to calculate due to negative electron affinity of EC